Synthesis and Characterization of ZnO based Buffer Layers for Thin Film Hetero Junction Solar Cell using Chemical Bath Deposition

A Synopsis

For Ph.D Program

by

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1. INTRODUCTION

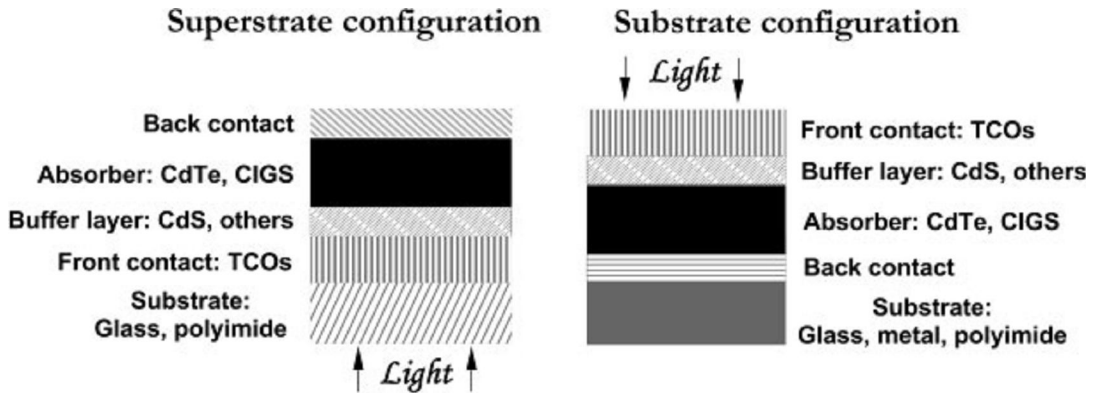
The search for renewable sources of energy is a major thrust area as an alternative to conventional energy sources due to high emission levels of green house gases like CO_2, CO, SO_2, P_2O_5 and acidification caused by the traditional fossil fuels. Furthermore, the cost of using non-renewable energy is increasing drastically. The social and environmental costs, such as the cost for securing reliable oil supplies, the cost to process nuclear wastes, and the cost to relief disasters caused by global climate changes etc, are increasing rapidly. So the need of the hour is to replace these conventional sources with non conventional one. Among the various renewable energies, solar energy is considered as the most propitious for its versatility, since solar energy does not pose location restrictions nor does it require special geographical features. Moreover the solar irradiation striking on the earth's surface is free of cost, clean, environmental friendly, endless in supply and widely distributed over the entire world. So the conversion process of this solar energy directly into electricity using the optical and electronic properties of suitable materials[photovoltaic effect]appears to be an elegant energy conversion process and an ideal alternative to conventional energy sources. Solar cells are considered as an appropriates candidate for obtaining energy from the sun since they can convert sunlight directly to electricity.

Solar cells furnish the most important long duration power supply for satellites and space vehicles. Traditional solar cells are expensive due to the cumbersome manufacturing processes, which often require vacuum chambers or high temperature heat treatment facility. In order to overcome such problems associated with the traditional solar cells, researchers came forward with flexible thin film solar cells and solar pastes. Thin film solar cells have several advantages over crystalline silicon cells. These cells are stable, lightweight, flexible, and durable. The quantity of materials required for fabrication of thin film solar cells is less because the thicknesses of the active layers are only a few micrometers. Therefore, impurities and crystalline imperfections can be tolerated to a much higher extent as compared to crystalline silicon.

A thin film is a layer of an inorganic or organic material which is deposited or grown using various growth processes on a substrate. The structural, chemical and physical properties of such deposited materials are strongly dependent on the deposition technique as well as on the thickness. Thin films can be fabricated by a variety of vacuum and non-

vacuum methods on inexpensive substrates such as glass. Also curved and/or flexible substrates such as polymeric sheets can be used, leading to lighter modules. Furthermore, composition gradients can be formulated in a more easily controllable manner. With the flexibility to accommodate irregular shapes and sizes, it allows applications on remote and portable devices, as well as integration to building structure.

A solar cell is a junction device obtained by placing two electronically dissimilar materials together with a thin electronic barrier in between to separate the charges (Chopra *et al.* 2004). Thin film solar cells consist of layers of different materials in thin film form. In fact, the solar cell consists of a substrate to hold on the thin film layers, transparent conducting oxide(TCO) to draw the current to outer circuit, buffer layer to create the junction with the absorber layer, so as to reduce absorption losses and to drive the generated carriers to the electrode, absorber layer for generating carriers on absorbing light with minimal transmission or reflection losses and metal contact layer as the bottom electrode. Each material has different physical and chemical properties and affects the overall performance of the device.



In the present investigation emphasis will be laid to fabricate thin film buffer layer for thin film heterojunction solar cells. The primary function of buffer layer in a heterojunction is to form a junction with the absorber layer while admitting a maximum amount of light to this layer (Mccandless *et al.* 1991**)**. For high optical throughput with minimal resistive loss the band gap of the buffer layer should be as wide as possible, with minimum possible thickness to maintain low series resistance. Efficiency gain of the thin film solar cells greatly depends upon the quality and thickness of the buffer layer. The standard CIS solar cell requires optimized thickness of buffer layer between the absorber layer and the transparent

front contact layer to improve efficiency. It drives out the photo generated carriers with minimal losses while coupling light to the junction with minimum absorption losses, yielding a highly efficient solar cell. Thin film heterojunction solar cells provide more light towards the junction if they have wide band gap buffer layer, in contrast with optimal low band gap absorber layer. This provides the most reliable way of increasing the efficiency of the solar cell.

The beneficial effects of the buffer layer ranges from modifying the absorber surface chemistry to protecting the sensitive interface during the subsequent window deposition process (Sterner *et al.*2004**)**. Favorable properties of the interface are suggested to be related with respect to lattice parameters. Interestingly the oldest and most well studied buffer layer material is CdS. But people are now trying to avoid cadmium containing materials due to the expected environmental risks arising from implementation of a CBD CdS process in a CIGS module production line (Hynes *et al*. 2000). Also the prohibition of cadmium in electrical or electronic equipment by legal regulations in different countries, can be a marketing problem for Cd-containing CIGS-based thin-film modules (Directive 2002/96/EC of the European parliament Jan 2003).The objective of the present study is to replace Cd with ZnO using a technique which is simple and suitable for large area deposition for industrial application.

2. REVIEW OF LITERATURE

Thin film fabrication is a promising technology of the future. A colossal volume of work is being carried out on thin film solar cells. Buffer layers play an important role in optimizing open circuit voltage in all types of thin film solar cells. The benefit of the buffer layers further enhances as their use decrease minority-carrier recombination losses from the absorber or base layer. Better results are expected, using a buffer layer with wider band gap material without band alignment for minorities and with aligning band for the majorities(Roedern *et al.* 1999). A secondary benefit of this type of layers, when used near the top of a cell, is optical enhancement because of reduced absorption and reflections losses. In the field of thin film solar cells, CIGS has acquired an important place as improved energy conversion efficiency about 20.3% has been reported recently (Jackson *et al*. 2011) as compared to earlier reported efficiency of 19.5% (Contresas *et al*. 2006). Most of the CIGS solar cells are fabricated using CdS buffer layer in order to protect junction region(cover the lattice mismatch) or to modify the surface of CIGS layer(Contresas *et al*.2005). As discussed above it is advisable to find an alternative to Cd material which is less or non toxic,

environment friendly and feasible for industrial application. More over, the efficiency of a CdS/CIGS solar cell reduces at short wavelengths due to loss of optical absorption from the CdS layer (Feilong *et al*.2008). ZnS,ZnSe,ZnO,MgO,SnO_2,$In(OH)_2$, In_2S_3 are the name of a few materials which were tested as an alternative to CdS buffer layer. The motivation for searching this alternative is to eliminate the toxic cadmium and also to improve the light transmission in the blue wavelength region. Since ZnO has a wider band gap and an enhanced response in the short wavelength of the spectrum is observed (Ennaoui *et al*.1998), so it may be a good alternative for Cd for buffer layer in the thin film solar cell.

ZnO is one of the most studied materials of the II-VI oxide materials that derive continuous attention of the researchers worldwide since last many decades **(**Bunn 1935). ZnO being a transparent electrode material and possess good material properties as compared with Indium tin oxide, is a good choice in photovoltaic cells (Fahrenbruch *et al.* 1983, Eberspacher *et al.* 1986**).** It is an n-type semiconductor with a direct wide band gap of 3.37 eV at room temperature, having optical transparency in the visible range (Wang *et al*. 2004). Sensing the potential of ZnO as an inexpensive, non toxic, transparent for visible light, wide band semiconductor, it can be chosen as a strong candidate for buffer layer in thin film solar cells as a substitute for CdS.

Several techniques have been used to fabricate ZnO thin films such as Atomic Layer Deposition, Chemical Bath Deposition, Sputtering, Metal Oxide Chemical Vapour Deposition, Electro-Deposition, Ion Layer Gas Reaction etc (Haricos *et al*. 2005). Among the different methods available to deposit thin films of semiconductors, chemical bath deposition (CBD) appears to be the simplest and cost effective technique. CBD refers to depositions from solution (usually aqueous) where the required deposit is both chemically generated and deposited in the same bath. CBD is widely used for deposition of various metal chalcogenide thin films. In chemical bath deposition process, precipitation of the solid phase occurs due to the super saturation in the reaction bath In a process of precipitation, at a given temperature the formation of a solid phase in the solution should start when the ionic product exceeds the solubility product constant ,which depends on the temperature and pH of the solution (Mane *et al*. 2000**).** Whereas, if the ionic product is less than the solubility product, then the solid phase produced will dissolve back to the solution resulting in no net precipitation. This forms the basic principle behind any chemical deposition process or in other words, the principle of CBD technique is to control the chemical reaction so as to effect the deposition of a thin film

by precipitation. CBD produces good deposits on suitable substrates by the controlled precipitation via hydrolysis and/or condensation reactions of metal ions and/or complexes from aqueous solution (O'Brien *et al.* 1998).

Chemical bath deposition (CBD) technique offers many advantages over other well-known vapour phase synthetic routes. It may control the growth factors such as film thickness, deposition rate and quality of crystallites by varying the pH of the solution, temperature and concentration of the precursors (Sankapal *et al.*2004). It does not require high voltage equipment, performs at room temperature and hence it is inexpensive. The only requirement for this deposition route is an aqueous solution consisting of a routine common chemicals and a substrate for a film to be deposited. It often suffers from a lack of reproducibility in comparison with other chemical processes; however, by the proper and careful optimization of growth parameters, one can achieve reasonable reproducibility. The film grown by one step process gives adherent compact films as compared to SILAR (Ennaoui *et al.*1998). Using different substrate with identical baths, yields different morphologies (Yamabi *et al.* 2002). It is suggested that H_2O_2 should be used to prepare polycrystalline phase with good optical transmittance (Ortega *et al.* 2003). Mikami *et al.*(2003) deposited thin films on CIGS thin films and fused silica glass from an aqueous solution with ethylenediamine or ammonia. The films grown with ethylenediamine showed a quite poor adhesion and uniformity as compared to the films grown with ammonia which showed a good adhesion and uniformity. The annealing of CBD-ZnO after the CBD process was also effective in the improvement of cell efficiency. The method offers to easily control the growth factors such as film. Ligands are employed to keep the free Zinc ion concentration low. Raising the bath temperature promotes some dissociation of the zinc complex, leading to controlled super saturation of the free metal ion. Acicular ZnO morphologies are best obtained by limiting the concentration of one of either Zn^{2+} or OH^- ions in the presence of excess of the other. The presence of a prior ZnO layer can facilitate nucleation at lower levels of super saturation and enable size tailoring of ZnO columns. The point at which the substrate is introduced into the bath is crucial and can lead to a significant difference in both the width of the rods and optical transparency of the films (Govender *et al.* 2004**).** Hexamine can be used as a shape inducing molecule and highly anisotropic nano wires (aspect ratio >150) with diameter ~30nm and lengths exceeding several microns after a 24 h growth period at 60-95^oC are reported (Sugunan *et al.* 2006**).**

Hodes (2007) discusses the factors which control crystal size, for example low temperature will slow down the redissolution of nuclei which increases the chance that a sub-critical nucleus will eventually grow to a stable size rather than redissolve. Kinetic stabilization of small nuclei results in a great total density of nuclei and therefore smaller crystal size, since the total quantities of reactants is fixed. Cluster mechanism results in smaller crystal size than the ion by ion mechanism. Thick films with a smaller crystal size can be formed by depositing on an existing thin film from a new solution and repeating this to the desired thickness. Annealing is a post-deposition method of increasing crystal size which depends on temperature and time of annealing as well on the material annealed and on the annealing atmosphere. Due to smaller size of CBD nanocrystals, they show size quantization and emission yield of CBD are normally low. He further reported that porosity may also be a function of substrate. The morphology of nano particles in CBD can be changed by changing various factors. For example, in CBD ZnO, which tends to grow as hexagonal pillars, if left to age in the deposition solution, has been shown to form hexagonal tubes due to preferential dissolution of the Zn basal plane.

Transmittance of the developed buffers was greatly increased integrating Cd free wide-band gap $In_x(OH, S)y$ and $ZnS_x(OH)_yO_z$ compared to standard CdS(Ahn *et al.* 2008). CBD - ZnO thin films using complexing agents, i.e., NH_3, Ethanolamine, Methylamine, triethanolamine(TEA) and Dimethylamine (DMA). TEA and MA showed highly resistive and very good transmittance quality of films (Khallaf *et al*. 2009). The pH value, counter-ion as well as heat treatment of seed layer can lead to significant difference in the crystal size and electrical resistivity of the films (Chu *et al*. 2009). Substrates show hydrophilic properties by dipping in a solution of $SnCl_2$/HCl for at least one hour. Diameter, length and density increase with increasing Zn^{2+} concentration. The average diameter and length of nanorods by two steps method is much smaller than that of the thin films by chemical bath deposition, which produce high quality ZnO nanorods thin films (Jia *et al*. 2010). Kokotov and Hodes (2010)reported ZnO/CdS composite films from a solution containing a mixture of Zn and Cd salts and thiourea. The nature of the film is very different if the substrate is seeded, either in situ (by adding Fe to the MEA with a final deposition solution Fe content of down to 0.75 ppm) or by permanganate substrate activation. CdS/ZnO composite, rather than CdS/ZnS, is obtained for mixed Cd-Zn deposition when the concentration of NH_3 is less than 0.5 M Offiah *et al.* (2010) used polyvinyl alcohol (PVA), polyvinylpyrrolidon (PVP) and distilled water to fabricate ZnO films. The transmittance of the as-deposited zinc oxide thin films

using the PVP medium is considerably higher than those of the PVA and H_2O deposition media. Wang *et al.* (2011) reported ZnO-Ag composite thin film using solution of silver nitrate and hexamethylenetetramine showing that silver particles grew on glass substrate, not on ZnO rods. Transmittance of composite film was found to be decreased as compared to pure ZnO. Intensity of the near band edge emission peak increases while that of the blue emission peak decreases due to the surface Ag nanoparticles plasmon resonance Hexagonal prisms, plates and rose-like twinned crystals were fabricated using chemical bath deposition with different concentration of gelatin (Duan *et al.* 2011). Oxalic acid and urea can be used as two complexing agents with band gaps of the order of 3.6 eV and 3.45 eV. Oxalic acid reduces the particle size more efficiently than urea **(**Ketabi *et al.* 2011).

3. GAPS IN THE KNOWLEDGE

From literature reviewed of it is clear that not much successful work has been reported to substitute CdS buffer layer with CBD-ZnO thin buffer layer. For an extensive use in commercial application pure and doped ZnO must be prepared at much lower temperature. Therefore it is necessary to develop a low temperature, large area deposition technology for the growth of ZnO films. More careful post annealing treatments as well as in situ doping of CBD-ZnO films using group III elements, such as aluminum, indium or gallium may reduce the resistivity further. Also the transmittance of CBD-ZnO films needs to be further improved. The smooth film of ZnO need to be prepared using either prior seed layer deposition or treatment like heating the substrate before inserting in the bath or to dip in $SnCl_2$/HCI solution to develop hydrophilic properties. An attempt will be made to deposit thin films based on the various complexing agents and study their effects on the structural and optical properties of the thin films. These complexing agents may be used to control quantity of zinc ions in the bath that improves the quality of ZnO buffer layer.

4. OBJECTIVES

1. To deposit ZnO thin film using different complexing agents via Chemical Bath Deposition route and optimization of different parameters like substrate, temperature, concentration of precursors, pH etc.
2. To perform characterization of deposited ZnO thin films using XRD, Electron Microscopy, Transmittance using UV Visible Spectrophotometer and Photoluminescence measurement using Spectrofluorometer.

3. To study the electrical properties of as prepared thin films.

5. METHODOLOGY

For the deposition of ZnO thin films via chemical bath deposition technique following methodology will be adopted:

1. Deposition of seed layer of ZnO using a wet chemical method.
2. Fabrication of ZnO thin film using Chemical Bath Deposition with different complexing agents.
3. Annealing of deposited thin films at different temperatures.
4. Characterization of thin films using XRD, Electron Microscopy, UV-visible, absorption & reflectance spectroscopy, and the electrical properties will be studied.

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